비냉각 검출기를 위한 BSCT 후막의 제작과 특성 분석

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The fabrication and analysis of BSCT thick films for uncooled infrared detectors

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Abstract - $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ (BSCT) thick films doped with 0.1 mol% $MnCO_3$ and Yb_2O_3 (0.1~0.7 mol%) were fabricated by the screen printing method on the alumina substrate. And the structural and electrical properties as a function of Yb_2O_3 amount were investigated. The lattice constants of the BSCT thick film doped with 0.1 mol% is 0.3955 nm. The specimen doped with 0.7 mol% Yb_2O_3 showed dense and uniform grains with diameters of about 6.3 mm. The thickness of all BSCT thick films was approximately 60 mm. The Curie temperature of the BSCT specimen doped with 0.1 mol% Yb_2O_3 was 18°C, and the dielectric constantand dielectric loss at this temperature was 4637 and 4.2%, respectively. The BSCT specimen doped with 0.1 mol% Yb_2O_3 showed the maximum value of $349X10^{-9}$ C/cm^2K at Curie temperature. The figure of merit F_D for specific detectivity of the specimens doped with 0.1 mol% Yb_2O_3 showed the highest value of $10.9X10^{-9}$ Ccm/J.

1. 서 론

Perovskite based materials are widely used in technical applications. Multilayer ceramic capacitor (MLCC), semiconductors with positive temperature coefficient of resistance (PTCR) and pyroelectric detectors are some of the versatile possibilities of applications [1,2]. $BaTiO_3$ is one of the most used dielectric materials and therefore often an object of research. Doped $BaTiO_3$ and solid solutions with e.g. $SrTiO_3$ provide new properties of ceramic materials. In particular, the polarization and dielectric constant change rapidly near the cubic-tetragonal $BaTiO_3$ phase transition, which makes this the most sensitive operation regime to defect infrared radiation. By partially substitution Sr^{2+} and/or Ca^{2+} ions at A-sites (Ba^{2+} ions) in $BaTiO_3$, one can set the temperature of the phase transition over a wide range [3]. For uncooled infrared detectors, this composition ratio is adjusted to allow operation near ambient room temperature.

Recently, the application of thick film technology to ferroelectric ceramics has been performed in a wide range of industrial field because of the simplicity and flexibility of thick film technology. Various thick film techniques, such as tape casting, sputtering, and screen printing method, can be used for successful deposition of thick films. Among these technologies, the screen printing method is one of the best for thick film preparation that involves high productivity and good cost performance brings the films to the stage of commercial mass production with typical thickness in the range of 5-100 mm, and the thick films effectively fill the technological gap between thin films and bulk ceramics. Moreover, compared to the thin film technology, the screen printing process should allow easier control of both the composition and homogeneity of the complex electronic ceramics.

A large number of rare earth additives have been successfully incorporated in the ABO_3 perovskite system of the ferroelectric ceramics to tailor the properties of these ceramics. In this study, $(Ba,Sr,Ca)TiO_3$ powders were prepared by the sol-gel method in order to decrease the phase transition temperature at around room temperature. And $(Ba,Sr,Ca)TiO_3$ thick films, doped with Yb^{3+} ions, were fabricated by a screen printing method to improve the dielectric properties. The structural and electrical properties, as a function of Yb_2O_3 contents, were examined for uncooled infrared detector applications.

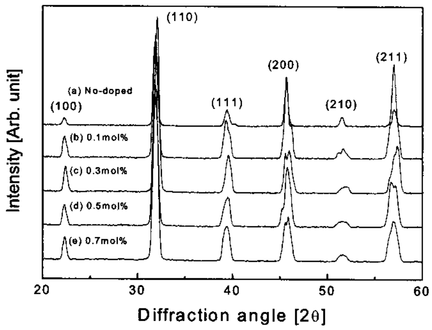
2. 실험 방법

The chemical compositions of the samples were given according to the following formula: $(Ba_{0.57}Sr_{0.33}Ca_{0.1})TiO_3$ + 0.1 mol% $MnCO_3$ + y mol% Yb_2O_3 (y= 0.1, 0.3, 0.5, 0.7). This BSCT composition gave a transition temperature near the ambient room temperature. Doped BSCT specimens with 0.1 mol% $MnCO_3$ were selected for their basic composition on the basis of previous experiments [4]. BSCT powders, started with a mixture of $Ba(CH_3COO)_2$, $Sr(CH_3COO)_2 \cdot 0.5H_2O$, $Ca(CH_3COO)_2 \cdot H_2O$ and $Ti[OCH(CH_3)_2]_4$ were prepared by the sol-gel method. Acetic acid and 2-methoxyethanol were used as solvents. Ba, Sr, and Ca acetates were dissolved in acetic acid, and then the solution was heated to 115°C for the evaporation of water. After cooling, Ti-isopropoxide, dissolved in 2-methoxyethanol, was added to the solution. The solution temperature was maintained at 60°C during refluxing. The powder precursors were dried and then calcined in a high-purity alumina crucible. The calcined powder, doped with Yb_2O_3 and $MnCO_3$, were mixed and ground by planetary ball millingfor 20h. The screen-printable pastes were prepared by kneading the ground BSCT powder with 30wt% of organic vehicle (Ferro. 75001). High purity alumina was used as a substrate. The bottom electrodes were prepared by screen printing method Pt paste and firing at 1450°C for 2hr. The processes of printing and drying were repeated 6-times to obtain a desired thickness. The coated thick films were sintered at 1450°C for 2 h in the closed alumina crucible.

The crystalline phase was identified by an X-ray diffractometry (Bruker,AXS D8 DISCOVER with GADDS, Germany). The surface and cross-sectional microstructure were examined by a field emitting scanning electron microscope (Philips, XL30 S FEG, Netherland). The average grain size was determined by the lineal intercept method. The dielectric properties of the specimens were measured suing LCR-meter (Fluke, PM6306, Germany). The pyroelectric properties were measured repeatedly using a digital electrometer (Keithley, 6514) at a constant rate of temperature change of 5 °C/min for increasing and decreasing temperatures in the ranged from -25°C to 60°C.

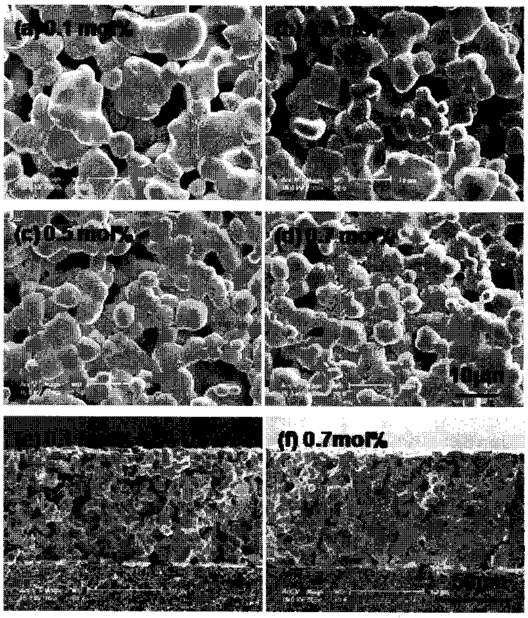
3. 결과 및 고찰

Figure 1 shows X-ray diffraction patterns of the BSCT thick films as a function of Yb_2O_3amount. All BSCT thick films showed the typical XRD patterns of cubic perovskite polycrystalline structure and no pyrochlore phase was observed. The lattice constants of BSCT specimens were independent of the Yb_2O_3 contents. This can probably be explained by the fact that the Yb^{3+} ions irregularly substituted for Ba^{2+}, Sr^{2+} and Ca^{2+} ions at the A-sites of ABO_3 perovskite structure. The lattice constants of the BSCT thick film doped with 0.1 mol%, 0.5 mol% and 0.7 mol% Yb_2O_3 are 0.3955 nm, 0.3978 nm and 0.3964 nm, respectively.



<Fig. 1> X-ray diffraction patterns of the BSCT thick films as a function of Yb_2O_3 amount

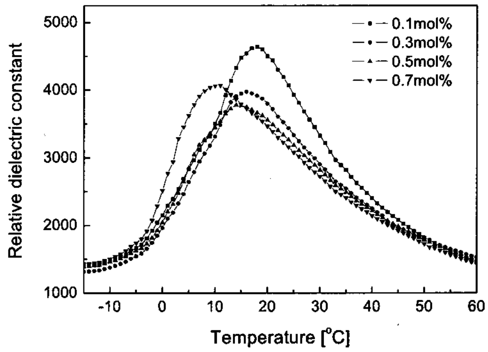
Figure 2 shows surface and cross-sectional SEM micrographs of the BSCT thick films as a function of Yb_2O_3 amount. The densification increased and average grain size decreased with increasing the Yb_2O_3 amount. This is due to the fact that Yb^{3+}ions act on the donor dopant in the BSCT specimens. The undoped BSCT thick films exhibited a porous microstructure with a grain size larger than 10 μm.



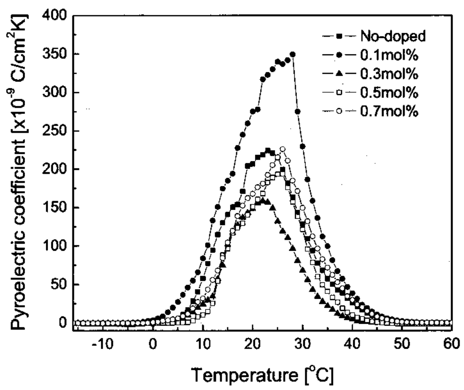
<Fig. 2> Surface and cross-sectional SEM micrographs of the BSCT thick films as a function of Yb_2O_3 amount

Figure 3 shows relative dielectric constant and dielectric loss of BSCT thick films as a function of temperature at 1kHz. The Curie temperature of the BSCT specimen doped with 0.1 mol% Yb_2O_3 was 18°C, and the dielectric constant and dielectric loss at this temperature was 4637 and 4.2%, respectively. The addition of Yb_2O_3 to BSCT specimens caused a decrease in the Curie temperature and the maximum dielectric constant, because it created cation vacancies in the lattice which is used for the maintenance of electroneutrality.

The BSCT specimen doped with 0.1 mol% Yb_2O_3 showed the maximum value of pyroelectric coefficient $349X10^{-9}$ C/cm^2K at Curie temperature in spite of their large pores because the specimen have the high dielectric constant and the large variation of the dielectric constant-temperature curve, as shown in Fig. 3.



<Fig. 3> Relative dielectric constant of BSCT thick films as a function of temperature at 1kHz



<Fig. 4> Pyroelectric coefficient of BSCT thick films as a function of temperature for the various Yb_2O_3 amount.

4. 결 론

In this research, BSCT thick films doped with $MnCO_3$ (0.1mol%) and Yb_2O_3 (0~0.7 mol%), were fabricated by the screen-printing method. All BSCT thick films showed the typical XRD patterns of cubic perovskite polycrystalline structure and no pyrochlore phase was observed. The densification increased and average grain size decreased with increasing the Yb_2O_3 amount. This is due to the fact that Yb^{3+}ions act on the donor dopant in the BSCT specimens. The BSCT specimen doped with 0.1 mol% Yb_2O_3 showed the maximum value of $349X10^{-9}$ C/cm^2K at Curie temperature in spite of their large pores.

[참고 자료]

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